

I. SOME EFFECTS OF THE STRUCTURE OF
DIENES ON THEIR POLYMERIZATION
II. THE SYNTHESIS OF MERCAPTANS

BY
FRED ERSKINE WOODWARD

A. B., Dartmouth College, 1943
A. M., University of Illinois, 1944

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
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PART ONE

SOME EFFECTS OF THE STRUCTURE OF DIENES ON THEIR POLYMERIZATION

INTRODUCTION

Substituted butadienes have been rather extensively investigated in the past.^{1,2,3} However most of the work was done before the mechanism of free radical polymerizations had been well established or before techniques of polymerization had been standardized.

The development in this laboratory of the technique of emulsion polymerization as well as its importance as a commercial method of polymerization has led to its use in this investigation.

DISCUSSION OF RESULTS

1,3-Cyclohexadiene has been prepared by a modification of the method of Rice and Stallbaumer⁴ in yields of 65 per cent from 1,2-cyclohexanediol diacetate by pyrolysis at $575 \pm 25^\circ$. Cyclohexadiene has been found to have a very slow rate of polymerization. This may be due in part to the difficulty of preventing the formation of cyclohexadiene peroxide which has been found to have a very high retarding activity in an emulsion polymerization of styrene and isoprene when present in very small amounts.

1,4-Dimethylbutadiene and 1,2,3,4-tetramethylbutadiene were both shown to have a much smaller retarding activity than 1,3-cyclohexadiene.

Polycyclohexadiene which is of necessity all *cis* in respect to the double bonds present is a powder. Its X-ray diffraction pattern indicates a degree of regularity intermediate between that of balata and unstretched natural rubber.

The copolymers of cyclohexadiene with styrene and acrylonitrile are also powders. The percentage of acrylo-

nitrile and cyclohexadiene in the copolymer approach a 1 to 1 ratio.

1-Phenylbutadiene has been prepared by the method of Von der Heide⁶ in a pure state, b. p. 80° (10 mm.) 61° (3 mm.), n_D^{20} 1.6114, m. p. 7-7.3°. Its rate of polymerization in a soap emulsion has been found to be 1.28 per cent per hour. The polymerization follows "zero order" kinetics.

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PART TWO

THE SYNTHESSES OF MERCAPTANS

INTRODUCTION

For the purpose of determining the modifier activity of tertiary mercaptans and also to enable the development of analytical methods for determining the composition and structure of commercial mixtures of primary, secondary, and tertiary mercaptans, the need arose for some pure secondary and tertiary mercaptans of known structure.

DICUSSION

3-Pentylmercaptan was prepared in 23 per cent yield from 3-bromopentane by treatment with thiourea and hydrolysis

of the resulting S-3-pentylisothiourea hydrobromide.^{1,2} Cyclopentyl mercaptan was prepared in 48 per cent yield by the same method.³

The following tertiary mercaptans were prepared by the "normal" addition of hydrogen sulfide to the corresponding olefin;⁴ tri-*n*-butylcarbinthiol in 14.4 per cent yield, dimethylnonylcarbinthiol in 44 per cent yield, and dibutylpropylcarbinthiol in 35 per cent yield. The method failed completely for the addition of hydrogen sulfide to 3-butyl-2-methyl-1-heptene.

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VITA

The writer was born in Brighton, Massachusetts, on August 30, 1921. He attended the public schools of Framingham, Massachusetts, and was graduated from Framingham High School in 1939. He entered Dartmouth College in the fall of 1939, receiving the degree of Bachelor of Arts, *cum laude*, on January 1, 1943.

In 1943 he entered the Graduate School of the University of Illinois, receiving the degree of Master of Arts in Chemistry in 1944. He was employed as a teaching assistant from February to June, 1943. Since September, 1943, he has held an appointment as Special Research Assistant in Chemistry on the Government Synthetic Rubber Program.



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